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## Canadian Patents Database

(12) Patent:

(11) CA 756165

(54) PIGMENTED FLUOROCARBON RESINS

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### ABSTRACT:

CLAIMS: [Show all claims](#)

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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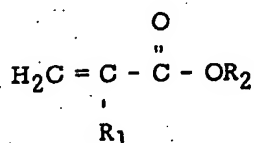
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This invention deals with a pigmented fluorocarbon polymer and is particularly concerned with a pigmented polyvinylidene fluoride resin having improved properties over those pigmented polyvinylidene resins obtainable heretofore.

Vinylidene fluoride polymers are recognized and used by the chemical industry and related industries as high performance corrosion resistance resins having a variety of uses. In many of these uses, which include fibers, films, coatings, extrusions and moldings, it is desirable to color the resin with pigments or other color additives. Unfortunately, many of those applications for polyvinylidene fluoride which require a white  $\text{TiO}_2$  pigment are restricted because  
 10 discoloration occurs under the relatively high thermal fabrication conditions to which polyvinylidene fluoride resins are subjected.

It has now been found that an improved  $\text{TiO}_2$  pigmented vinylidene fluoride resin is obtained by incorporating with the resin and pigment certain polyacrylate compositions. Thus, in accord with the invention there is provided a composition comprising polyvinylidene fluoride,  $\text{TiO}_2$  pigment, and from 1 to 50 percent by weight of said polyvinylidene fluoride of a polyacrylate derived from a monomer having the structure:



where  $\text{R}_1$  is selected from the group consisting of hydrogen and methyl and  $\text{R}_2$  is  
 20 alkyl containing from one to four carbon atoms. This invention also embodies the method of making the improved polyvinylidene fluoride compositions which comprises homogeneously blending polyvinylidene fluoride,  $\text{TiO}_2$  pigment, and from 1 to 50 percent by weight of said polyvinylidene fluoride of an acrylate polymer as above defined. Preferred compositions of the invention will contain from 1 to 25 percent by weight of the polyacrylate.

The procedure by which the improved compositions of this invention may be made will vary and may employ any one of the various techniques normally



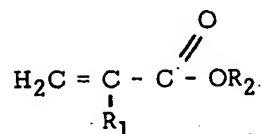
used to obtain intimate mixing of components. However, three techniques will be preferred for the operation of this invention and these will involve mechanical blending by means of (a) solid mixing, (b) dispersion mixing, and (c) solution preparation.

In the solid mixing technique, melt blending is a convenient method for obtaining intimate mixture of components. In this procedure, the polyvinylidene fluoride in pellet or other particulate form together with the  $\text{TiO}_2$  and acrylate polymer are blended at room temperature and fed to a heated extruder, Banbury mixer, or roller mill where the materials are hot blended. The blend may be  
10 shredded, ground, or extruded and pelletized and it may be delivered to any type of fabrication apparatus such as an extruder, the plenum chamber of an injection molding machine, etc.

In the second technique the ingredients may be milled, preferably by a ball mill to obtain a pigmented dispersion which is subsequently used for the formulation of films and coatings. In this technique a liquid vehicle will be employed which has solubility for the acrylate polymer, but in which the polyvinylidene fluoride is insoluble at room temperature. However, this solvent will have solvating properties for the polyvinylidene fluoride resin at elevated temperatures so that when the dispersion is subjected to baking after being applied as  
20 a coating or as a cast film, the polyacrylate and the polyvinylidene resin, together with the pigment will blend during the heating step into the uniform improved pigmented composition of the invention. Reference is made to copending Serial No. 941,047 which describes in more detail the preparation of polyacrylate vinylidene fluoride dispersions which procedures may be employed in the practice of this invention.

In the third technique ordinary coatings practices are followed to obtain a co-solution of the resins with the  $\text{TiO}_2$  suspended therein.

As indicated above the polyacrylate additive employed in this invention is derived from the monomer having the structure



wherein  $\text{R}_1$  is selected from the group consisting of hydrogen and methyl and  $\text{R}_2$  is alkyl containing from 1 to 4 carbon atoms. It will be understood that such acrylates will include homopolymers and copolymers, and will include the high molecular weight thermoplastic homopolymers of methylmethacrylate, methylacrylate, ethylacrylate, ethylmethacrylate, butylmethacrylate and the like and similar high molecular weight thermoplastic copolymers of such acrylates and methacrylates with other ethylenically unsaturated compounds wherein the comonomer makes up a minor proportion of the copolymer, preferably less than

10 about 25 mole percent and still more desirably less than about 10 mole percent. Suitable copolymers include for example, those obtained by polymerizing with the above acrylates and methacrylates a minor proportion of comonomers such as ethylmethacrylate, propylmethacrylate, butylmethacrylate, ethylacrylate, propylacrylate, butylacrylate, styrene, alpha methylstyrene and methacrylic acid. The thermoplastic homopolymers of methylmethacrylate and copolymers containing about 20 to 80 mole percent of another ethylenically unsaturated comonomer, as for example, a methylmethacrylate-ethylacrylate copolymer, are highly preferred in the practice of the present invention. It will be understood that small amounts (e.g. less than 5%) of other comonomers as for example

20 acrylic acid, methacrylic acid, and the like are frequently present in the above identified acrylate copolymers.

As indicated, the amount of acrylate present in the composition of the invention will range from about 1 to about 50% by weight of the polyvinylidene fluoride. It will be understood that the amount of acrylate used may vary with the specific end use of the product. For example, where extrusions are to be made with the products of the invention, the amount of acrylic present will be on the order of 10%, but on the other hand where coatings are to be made from the compositions and amount of acrylic from 1 to 25% will generally be used.

In order to further illustrate the invention, the following Examples are given. All parts given in the Examples are parts by weight.

#### EXAMPLE 1

A physical mixture of 450 parts of polyvinylidene fluoride powder, 50 parts of polymethylmethacrylate powder and 10 parts of  $\text{TiO}_2$  pigment were cold mixed in a blender and fed to a 24" long, one inch extruder equipped with a .060 inch diameter monofilament die. The extruder was heated at 400°F. on the feed zone, 425°F. on the breaker plate zone and 450°F. on the die tip. A smooth, glossy, bright white monofilament was obtained. At the conclusion of the run, the temperature of the die tip was increased to 500°F. A slight acrylic odor was produced, but no discoloration of the monofilament was observed. Under similar conditions when the acrylate is not present,  $\text{TiO}_2$  pigmented polyvinylidene fluoride badly discolors and fumes at 500°F.

The pigmented monofilament was chopped into pellets and compression molded at 400°F. into .020 inch thick sheets under a total load of 40,000 pounds. The sheets were compared with a similar formulation devoid of the polyacrylate. The polyacrylate stabilized sheet was bright, glossy and white while the sheet prepared from the mixture devoid of the polyacrylate had a definite yellow cast.

#### EXAMPLE 2

A pigmented composition was prepared by ball milling 49.9 g. of  $\text{TiO}_2$  and 20.5 g. of a toluene solution containing 40% by weight of a polymethylmethacrylate-ethylacrylate copolymer (about 60:40 mole ratio) with a polyvinylidene fluoride resin dispersion consisting of 146.4 g. of resin dispersed at a 46.8% by weight solids level in an 80:20 weight ratio mixture of dimethyl phthalate and diisobutyl ketone. The formulation thus contained a resin to pigment weight ratio of 75.6:24.4 and a weight ratio of polyvinylidene fluoride to polyacrylate of 94.7:5.3 (17.85:1).

For comparative purposes, the same polyvinylidene fluoride dispersion

was milled with  $\text{TiO}_2$  in the same proportion (25% by weight of resin) solids, but without the polyacrylate copolymer.

One hundred grams of each composition was diluted with 20 g. of a 60/40 weight dimethyl phthalate-diisobutylketone mixture. Hydrochloric acid-pickled cold-rolled steel panels were knife coated with each formulation to give a .010 inch thick wet film. The panels were removed from the oven and quenched in room temperature water. The panels coated with the polyvinylidene fluoride-polyacrylate composition were smooth, glossy and white while the pigmented polyvinylidene fluoride composition devoid of the polyacrylate had yellowed and lacked a smooth glossy surface.

### EXAMPLE 3

1050 g. of ground polyvinylidene fluoride powder, 138 g. of a 40% by weight solution in toluene of a polymethylmethacrylate-ethyl acrylate copolymer, 1084 g. of dimethyl phthalate and 271 g. of diisobutyl ketone were charged to a ball mill jar. Nineteen pounds of Burundum cylinders  $\frac{13}{16}$ " x  $\frac{7}{8}$ " were added and the jar was rotated at 24 r.p.m. for 16 hours.

The formulation was filtered through four layers of 90 x 90 cheesecloth. Its viscosity (Brookfield LVT - no. TE spindle, 3 r.p.m.) was 9,300 cp. Hegman grind rating was 5.

150 g. of the dispersion was mixed with 63 g.  $\text{TiO}_2$  pigment and passed three times on a 2-1/2 x 5 in. three roller mill. 47.7 g. of the resulting paste was added to 336 g. of the dispersion to give a 50.6% solids white dispersion baking enamel.

This baking enamel was sprayed onto 4" x 12" aluminum panels and baked 20 minutes at 204°C. in a circulating hot air oven. The coating was hard, white and 0.001 to 0.0015 inch thick. The coating remained tightly adherent with excellent chalking resistance after one year's 45° south exposure at King of Prussia, Pennsylvania. The coating was excellently formable showing no signs of peeling

or cracking on bending on a radius of 0.020 in. The toughness of the coating was evidenced by its ability to withstand repeated bending which cracked the aluminum substrate panel. The coating had a pencil hardness of 3H and withstood 2 hr. boiling in water with no loss of adhesion or changes in properties.

Coated panels were unaffected by a 1000 hr. exposure in a salt spray cabinet. The coatings were slightly stained in exposures at 80°C. to 5% sodium hydroxide and 5% hydrochloric acid solutions.

#### EXAMPLE 4

Following the method of Example 3, a coating formulation was made  
10 containing:

600 wt. parts of ground polyvinylidene fluoride

375 wt. parts polymethylmethacrylate-ethylacrylate solution (40%  
solids in toluene)

1200 wt. parts dimethyl phthalate

300 wt. parts diisobutyl ketone

450 g.  $\text{TiO}_2$  pigment

300 g. ZnO pigment

Solids content - 47%

Resin/pigment ratio - 50/50

20 Brookfield LVT viscosity (TE spindle, 3 rpm) was 50, 464 cp.

Particle size (microscopic) - 75% < 3 microns, 95% < 5 microns

Hegman grind - 6

The coating was applied to aluminum panels and baked as in Example 3.

The same properties were obtained as in Example 3 but with an increase in hiding power.

#### EXAMPLE 5

A mixture of 50 wt. parts polyvinylidene fluoride, 50 wt. parts intermediate molecular weight methylmethacrylate (viscosity at 30% w. in cellosolve

acetate at 250° - 800 cp.), and 100 wt. parts  $\text{TiO}_2$  pigment were melt blended at 325°F. on a steam heated two roll mill as described below.

This 50% w. pigment composition was prepared for use as a stabilized "pigment concentrate" in extruding electronic wire insulation. In practice, chips of the "super concentrate" described below are mixed with 24 times their weight of natural plastic pellets and co-extruded to give a so-called "2% concentrate". This in turn is further mixed with natural plastic to give the desired hiding power or color intensity.

The materials were first mixed in the powder form in a laboratory blender. They were then milled on a 2 roll (3" diameter) rubber mill steam heated to 325°F. After a homogeneous rolling bank was obtained, the mix was sheeted off in a 1/16 to 1/8" thick sheet. This was chipped in a regrinder to approximately 1/4 in. chips. The chips were compression molded at 400°F. and 40,000 pounds total load. Chrome plated brass "squeegee" plates were used as a surface on which to obtain tough, white, smooth-surfaced 0.020 inch thick white sheet. Strong adhesion to the plates was observed.

Similar control sheets prepared devoid of acrylic resin were brittle, porous, and discolored.

#### EXAMPLE 6

This example shows the use of acrylic resins in maintaining the whiteness of solution type pigmented polyvinylidene fluoride coatings and films.

A mixture containing:

12% w. polyvinylidene fluoride powder

20% w. triethyl phosphate

40% w. dimethyl acetamide

8% w. xylene

10% w. acrylic polymer solution

(4% solids of polymethylmethacrylate-ethylacrylate



copolymer in 6% toluene)

was heated at 80°C. and stirred until complete solution was obtained. The solution was charged to a ball mill jar along with 10% w. TiO<sub>2</sub> pigment.

This gave a 75/25 polyvinylidene fluoride to acrylic ratio, a 62/38 resin to pigment ratio, and a 26% solids pigmented solution.

The ball mill jar was rotated as in Example 3.

The viscosity of the solution was 2100 cp. (Brookfield LVT-No. 3 spindle 6 rpm). A Hegman gage reading of 7 was obtained.

10 Films of the solution were cast on tempered plate glass using a .010 in. clearance doctor blade. The films were baked in a circulating air oven 30 min. at 175°C. Tightly adherent, white, glossy, 0.001 in. thick coatings resulted. When the procedure was repeated using a mold release agent on the glass, tough, white, 0.001 in. thick films were obtained by stripping the baked coating from the glass plates.

#### EXAMPLE 7

Example 2 was repeated using a Hunter reflectometer to distinguish the improvement in whiteness of polyvinylidene fluoride coatings containing acrylic resins.

20 Aluminum panels were used as standard substrates on which coatings were sprayed. The coating thickness was 0.001 in. after baking.

The percent reflectance of each coating was measured using a blue filter and a green filter in accord with standard practice. The values obtained are shown in the following table. The lower the reflectance value the darker the specimen. A difference of 1 percentage point is significant in that it is visible to the naked eye.

TABLE

% Reflectance

Coating composition	% Reflectance	
	(blue filter)	(green filter)
A. 18% $\text{TiO}_2$ in 95/5 wt./wt. polyvinylidene fluoride/polymethylmethacrylate on chromate treated aluminum	80.5	86.5
10 B. 18% $\text{TiO}_2$ in polyvinylidene fluoride on chromate treated aluminum	71	80

It is clear from the above table that the use of the polymethylmethacrylate imparts a very significant improvement to the composition.

EXAMPLE 8

A rapid qualitative whiteness standard was established to rate the whiteness of molded polyvinylidene fluoride sheet. To do this color chips of 01 Porcelain White (Ferro Corporation) were indexed as 10 on the rating scale; color chip a of the Color Harmony Manual, Container Corporation of America was indexed 20; and the white (light limit) standard of Military Standard 104, 20 supp. no. 1 was indexed 100.

Molded sheet was prepared by incorporating in separate samples 2% by wt. zinc oxide; 2% zinc sulfide; 2% antimony oxide; 2% titanium dioxide (rutile); and 50% titanium dioxide into polyvinylidene fluoride specimens on a steam heated two roll mill at 325°F. A similar 2%  $\text{TiO}_2$  composition was made by blending 10 wt. parts  $\text{TiO}_2$  pigment into a 9/1 weight mixture of polyvinylidene fluoride and polymethylmethacrylate on the mill at 325°F.

The milled compositions were sheeted off the mill in 1/8" thick sheets and 0.20 in. thick sheets were compression molded at 400°F. under a total load of 40,000 pounds.

30 The resulting sheets were subjected to color comparisons. The lower the value the whiter the sample. The samples were color rated from whitest to

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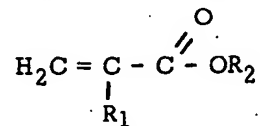
most cream colored as follows:

<u>Sample of Polyvinylidene fluoride containing -</u>		<u>Color Value</u>
2% $\text{TiO}_2$ and polymethyl- methacrylate		5
2% $\text{TiO}_2$		40
2% $\text{ZnS}$		8
2% $\text{ZnO}$		25
2% Antimony oxide		30
10 50% $\text{TiO}_2$		75

It is clear from the above that the methacrylate containing composition is vastly superior to the specimens without it and it is also clear that the whiteness of the composition of this invention is 2.5 times whiter than the primary standard (01 Porcelain White - rating 10).

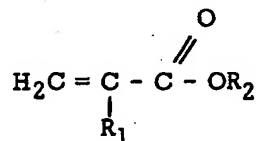
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition comprising polyvinylidene fluoride,  $\text{TiO}_2$  pigment and 1 to 50 percent by weight of said polyvinylidene fluoride of a polyacrylate derived from a monomer of the structure



where  $\text{R}_1$  is selected from the group consisting of hydrogen and methyl, and  $\text{R}_2$  is alkyl containing from one to four carbon atoms.

2. A composition comprising polyvinylidene fluoride, titanium dioxide, and from 1 to 50 percent by weight of said polyvinylidene fluoride of a polymer consisting essentially of polymethylmethacrylate.
3. A composition having improved color stability comprising polyvinylidene fluoride, titanium dioxide and from 1 to 25 percent by weight of said polyvinylidene fluoride of a polymethylmethacrylate.
4. A composition having improved color stability comprising polyvinylidene fluoride, titanium dioxide and from 1 to 25 percent by weight of said polyvinylidene fluoride of a copolymer of methylmethacrylate and ethylacrylate.
5. The method of making a  $\text{TiO}_2$  pigmented polyvinylidene fluoride having improved color stability which comprises blending polyvinylidene fluoride,  $\text{TiO}_2$ , and from 1 to 50 percent by weight of said polyvinylidene fluoride of a polyacrylate derived from a monomer of the structure



where  $R_1$  is selected from the group consisting of hydrogen and methyl, and  $R_2$  is alkyl containing from one to four carbon atoms.

6. The method of Claim 5 wherein the polyacrylate is polymethylmethacrylate.

7. The method of making a  $TiO_2$  pigmented polyvinylidene fluoride having improved color stability which comprises blending polyvinylidene fluoride,  $TiO_2$  and from 1 to 25 percent by weight of said polyvinylidene fluoride of polymethylmethacrylate.

8. The method of making a  $TiO_2$  pigmented polyvinylidene fluoride having improved color stability which comprises blending polyvinylidene fluoride,  $TiO_2$  and from 1 to 25 percent by weight of a copolymer of methylmethacrylate and ethylacrylate.